Polymer Chemistry

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Cite this: *Polym. Chem.*, 2013, **4**, 3959

Ruthenium catalyzed equilibrium ring-opening metathesis polymerization of cyclopentene†

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Received 8th May 2013
Accepted 29th May 2013

DOI: 10.1039/c3py00584d

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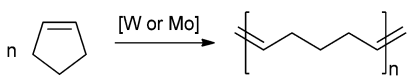
Polypentenamer was synthetized by equilibrium ring-opening metathesis polymerization (ROMP) using well-defined ruthenium catalyst systems. It was found that the equilibrium time is influenced by the catalyst loading or the catalyst activity, however as expected, the overall cyclopentene conversion is determined only by the applied reaction temperature. Equilibrium of the growing chain and monomer was observed and the activation enthalpy and entropy were determined as: $\Delta H = -5.6$ kcal mol^{-1}; $\Delta S = -18.5$ cal mol^{-1} K^{-1}. So far these values are the lowest which are reported for cyclopentene polymerization catalyst systems. This unique feature of the equilibrium polymerization opens a way for the synthesis of durable, environmentally friendly elastomers where tires can be not only synthetized but also readily recycled by the same transition metal catalyst system.

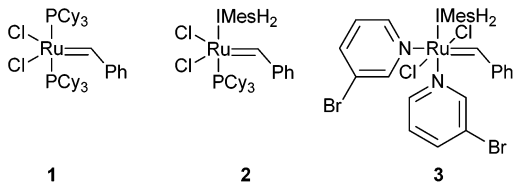
Introduction

The *trans*-polypentenamer has unique relevance among the synthetic rubbers since it has similar physical properties to natural rubber.[1,2] The polypentenamer additives have a propitious effect on the tire properties and have been studied extensively for this application.[1–3] The molybdenium ($MoCl_5$/$Al(C_2H_5)_3$) and tungsten (WCl_6/$Al(C_2H_5)_3$) catalyzed ring opening metathesis polymerization of cyclopentene was first investigated by Natta and Dall'Asta (Scheme 1).[4] The polymerization enthalpy for the WCl_6/$Al(C_2H_5)_2Cl$ system was investigated by Kranz and Beck and found to be -4.2 kcal mol^{-1} for *trans* and -3.2 kcal mol^{-1} for *cis*-polypentenamer. -4.5 kcal mol^{-1} was reported for polypentenamers containing 65% *trans* double bonds.[5] Similar data were reported later by Lebedev.[6]

The thermodynamic study using WCl_6/$Al(C_2H_5)Cl_2$ catalysts revealed that the cyclopentene conversion does not depend on the catalyst activity but the reaction temperature.[7] This observation indicated characteristic monomer–polymer equilibrium. Negative activation parameters have been found indicating higher performance at lower reaction temperature. The equilibrium thermodynamic data have been found as $\Delta H = -4.4$ kcal mol^{-1}; $\Delta S = -14.9$ cal mol^{-1} K^{-1}.[7,8] Since then, many other transition metal catalyst systems have been developed as efficient cyclopentene polymerization catalysts.[9–12,16,18] Yet the ruthenium catalyzed cyclopentene polymerization studies are rare. There are only a few examples for ruthenium based catalyst systems such as $RuCl_2$(*p*-cymene)(PR_2R')[9] and carbynehydridoruthenium[10] complexes. The ring-opening metathesis polymerization of cyclopentene using well defined catalysts **1**[11] and **2**[12] has also been reported (Scheme 2). The main advantages of the application of well-defined ruthenium catalysts compared to other reported systems (*i.e.* tungsten catalysts systems) are the relatively high catalyst stability, the elimination of co-catalyst or activators, and the lack of side reactions resulting from the high Lewis acidity of the older systems. The high catalyst stability, besides providing robust chemical processes, enables the design of easily separable and recyclable polymerization catalyst systems making the polymerization reactions clean and economic.[13] Thermodynamic studies on the ruthenium systems' catalyzed polypentenamer formation have never been completed. These catalysts provide an opportunity



Scheme 1 Ring-opening metathesis polymerization (ROMP) of cyclopentene.



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Scheme 2 Ru catalysts tested for cyclopentene ring-opening metathesis polymerization.

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† Electronic supplementary information (ESI) available: Additional data, experimental section, thermodinamic calculations, charts, GPC data and NMR spectra. See DOI: 10.1039/c3py00584d

to study the thermodynamics of the reaction without the complications of potential side reactions such as acid catalyzed oligomerization, impurities from catalyst generation, and metal based halogenations.

Herein we report a systematic thermodynamic investigation of the ruthenium catalyzed ring-opening metathesis polymerization of cyclopentene. This study also details the investigation of the influence of catalyst loading and type (**1**, **2** and **3**) on the polymerization reaction and polymer properties (Scheme 2).

Results and discussions

Thermodynamic investigations

The cyclopentene polymerizations were investigated at different reaction temperatures (0, 10, 20 and 30 °C) using constant catalyst loading (0.22 mol%) and monomer concentration (2.17 M) in toluene-d_8 solution. At the end of the reaction, the catalyst was quenched with ethyl vinyl ether and conversions were determined by ^{1}H NMR. It was found that the equilibrium could be achieved within two hours at 0 °C (conversion: 82.2 ± 1.6%; 82.4% after five hours). The ruthenium complex **2** catalyzed cyclopentene conversions/equilibriums are summarized in Table 1. Following the addition of cyclopentene monomer to the catalyst solution the viscosity of the mixtures continuously increased without a color change. Visually higher viscosities were observed for the polymerizations conducted at 0 °C and 10 °C. The conversions were determined by ^{1}H-NMR according to the integrals of the monomer (5.53 ppm) and the polypentamer (5.30 ppm) peaks. It was found that at each investigated reaction temperature the cyclopentene conversions were slightly higher (average: 5.7 ± 1.2%) than those of the reported tungsten ($WCl_6/Al(C_2H_5)Cl_2$) catalyst system.[7] The thermodynamic parameters were calculated to be: $\Delta H = -5.6$ kcal mol^{-1}; $\Delta S = -18.5$ cal mol^{-1} K^{-1} (Fig. 1). As in case of the $WCl_6/Al(C_2H_5)Cl_2$ system, lower conversion was observed at higher temperatures.

The *cis*/*trans* bond ratios were determined by quantitative ^{13}C NMR spectroscopy (130.7 ppm *trans*; 130.1 ppm *cis*).[14] It was found that the ratio of *trans* bonds in the polymer falls between 81.8% and 83.8% in the 0 °C and 30 °C temperature range (Fig. S2–S6†). Similar *cis*/*trans* bond ratio was reported for $WCl_6/Al(C_2H_5)Cl_2$ catalyst system (84% *trans* structure as equilibrium for polypentenamers at 0 °C). It is also known that *cis* selective catalyst $WF_6/(C_2H_5)AlCl_2$ gave high *cis* ratio even at high cyclopentene conversion.[15] In some cases the *cis* bond is dominant and can be as high as 80%.[16]

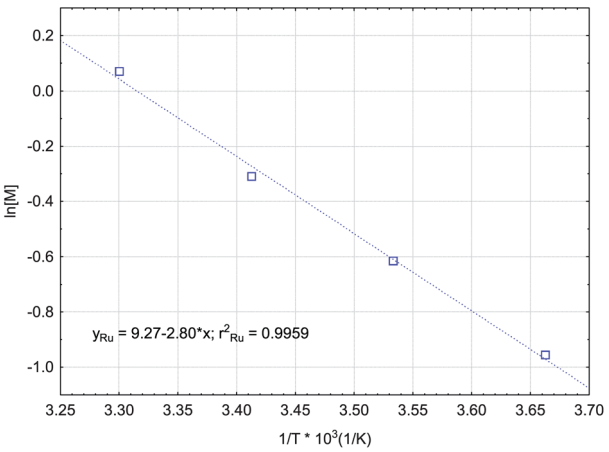


Fig. 1 Conversion and thermodynamics of cyclopentene's equilibration with its polymer. Toluene-d_8; [cyclopentene] = 2.17 M; 0.22 mol% catalyst **2**. t_r = 2 h.

In the present study, the influence of reaction temperature on the molecular weight (MW) and polydispersity index (PDI) have also been investigated. It was found that the molecular weight of the polymer significantly depends on the applied reaction temperature. At higher temperature lower polymer weight was observed. Interestingly, the molecular weight of the polymers synthetized at 0 °C is five times higher than theoretically calculated (Fig. 2), indicating that the propagation rate is much faster than the initiation rate, which is often observed for

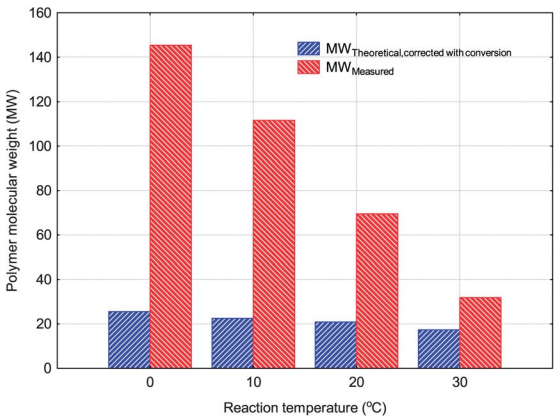


Fig. 2 Comparison of theoretical and measured MW (kDa) values of polypentenamers *vs.* reaction temperature. Toluene-d_8 solution; [cyclopentene] = 2.17 M; **2** loading = 0.22 mol%; t_r = 2 h.

Table 1 MW and PDI data of the polypentenamer synthetized at different reaction temperature. Toluene-d_8 solution; [cyclopentene] = 2.17 M; 0.22 mol% catalyst **2**

t (°C)	t_r (h)	Conversion (%)	MW^a (kDa)	MW^b (kDa)	MW^c (kDa)	PDI
0	2	82.2 ± 1.6^d	31.5	25.2	145.4	1.76
0	5	82.4	30.4	25.1	122.3	1.88
10	2	75.1	30.4	22.8	114.7	1.85
20	2	66.2	31.9	21.0	69.6	1.96
30	2	50.0 ± 1.4^d	31.9	16.5	31.8	2.07

^{a} Theoretically calculated. ^{b} Theoretically calculated and corrected with conversion. ^{c} Experimentally measured. ^{d} Average of four runs.

ROMP reactions using **2**.[17] The PDI values fall between 1.7 and 2.1 range (Fig. S2†). A slight increase can be observed at higher reaction temperature (Table 1 and Fig. 3).

A similar trend was reported for the W(CH-*t*-Bu)(N-2,6-C_6H_3-*i*-Pr_2)(O-*t*-Bu)$_2$ (**4**) (Scheme 3) catalyst system. Polymerization conducted at 25 °C resulted in polypentenamers with 1.5–1.8 PDI values, however at low reaction temperature (−40 °C) the formed polymers' PDI values dropped to 1.1–1.2.[18]

At longer reaction times, a lower molecular weight polymer with a higher PDI value was produced due to cross metathesis reactions.

Investigation of the influence of catalyst loading on the ROMP of cyclopentene

In the following experiments the influence of catalyst loading on the cyclopentene conversion and polymer properties was investigated. The test reactions were carried out at 0 °C reaction temperature in toluene-d_8 solution at constant monomer concentration (2.17 M), with a reaction time of two hours in each experiment. The impact of the catalyst (**2**) loading was investigated at 0.11–1.04 mol% range. It was found that the conversions were similar above 0.22 mol% catalyst loadings (82.2–83.7%). However, below this catalyst content more than two hours equilibration time is needed to achieve the equilibrium concentration at this condition. On the contrary, shorter gelation times were observed at higher catalyst loading (the stirrer stopped working in approximately 50 min at 1.04 mol% and at 70 min at 0.22 mol% catalyst loading) indicating rapid reactions to the equilibrium. The catalyst concentration had a large role in the ultimate molecular weight. The highest polymer molecular weight was found (156.7 kDa with 1.70 PDI values) when 0.54 mol% catalyst loading was used. It is worth mentioning that this value is approximately 15 times higher than the theoretically calculated (and conversion corrected) polymer molecular weight (10.62 kDa) based on the monomer/catalyst ratio. Significantly lower polymer weight (76.3 kDa) and slightly higher polydispersity (1.96) was observed at 1.04 mol% catalyst loading due to the higher extent of initiation and cross metathesis side reactions (Table S1†).

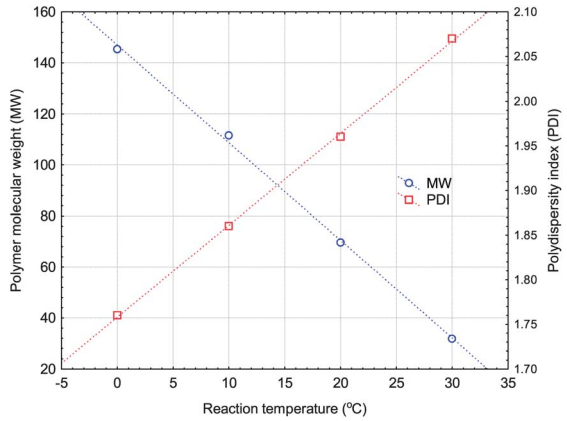
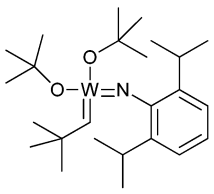


Fig. 3 Comparison of measured MW (kDa) and PDI values of polypentenamers *vs.* reaction temperature. Toluene-d_8 solution; [cyclopentene] = 2.17 M; **2** loading = 0.22 mol%; t_r = 2 h.



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Scheme 3 W catalysts tested for cyclopentene ring-opening metathesis polymerization at −40 °C.

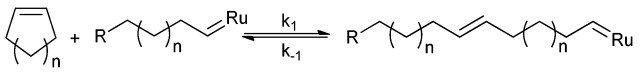
Investigation of the influence of various Ru catalyst systems on the ROMP of cyclopentene

The activity of different catalyst systems was investigated using constant cyclopentene (2.17 M) and catalyst (0.22 mol%) concentration. More than 70% conversion could be achieved for each catalyst after two hours at 0 °C. Lower conversion was observed for catalyst **1** (70.2%) with similar conversions observed for catalysts **2** and **3** (82.2 and 82.4%).

Although the conversions were similar, the gelation times were significantly different. In case of catalysts **1** and **2** the gelation times were approximately 70 min for **2** and slightly longer for **1**, however for catalyst **3** the gelation time was only 5 min. This indicates that the equilibration time is significantly shorter with catalyst **3** than **2** or **1**. The highest molecular weight polymer was observed for catalyst **2** (145.4 kDa) with 1.76 PDI value which is consistent with the slow initiation and rapid propagation of this system. Both catalysts **1** and **3** provided lower molecular weight polymer: 87.8 and 68.6 kDa. The PDI values were 1.70 for **1**, 1.76 for **2** and 1.89 for **3** (Table S2†). Past results have demonstrated that both the **1** and **3** catalysts have more favorable initiation rate/propagation rate for cyclopentene polymerization than catalyst **2**. However the overall reaction rate is slower for catalyst **1** than catalysts **2** or **3**. Consistent with past observations, for catalyst **3** both the initiation and the propagation steps seem to be faster than for the other catalysts. As the molecular weight of the synthesized polymers is significantly higher than the theoretical values, it is expected that in all cases the rate of the propagation step is faster than the rate of the initiation.

Mechanistic considerations

Ruthenium based alkene metathesis catalysts have been extensively studied mechanistically.[19] A phosphine must first dissociate resulting in a fourteen valence electron intermediate which reacts with the olefin and enters the catalytic cycle. Ring opening metathesis polymerization (ROMP) reactions are driven by the ring strain of the cyclic olefin since it is relieved in the polymerization. For example, it is not possible to ROMP cyclohexene as its ring strain energy is close to 0 kcal mol^{-1}; in contrast to the cases of norbornene or *trans*-cyclooctene having high ring strain energies (27.2 kcal mol^{-1} and 16.7 kcal mol^{-1}), and are readily polymerized.[17] In the equilibrium shown in Scheme 4, k_{-1} is faster than k_1 where using cyclohexene and slower where using *trans*-cyclooctene (Scheme 4). The ring



Scheme 4 Ruthenium catalyzed equilibrium polymerization of cycloolefines.

strain energy for cyclopentene is between the energies of cyclohexene and cyclooctene, 6.8 kcal mol^{-1}.[20] This energy value results in a condition where k_1 and k_{-1} are close to equal and due to the negative and moderately large ΔS, the equilibrium concentration of cyclopentene becomes extremely temperature dependent.

The copolymerization of cyclopentene with 5% strained olefin (norbornene) resulted in a small decrease in monomer concentration and did not result in a significant shift of the equilibrium. 60% cyclopentene conversion was observed in the absence and 63% in the presence of 5 mol% norbornene.[21] This observation reveals that the insertion of strained monomer into the polypentenamer chains does not result in a "lock" of the polymer chain and reduces the depolymerization leading to higher monomer conversion. At equilibrium and high molecular weights, the equilibrium constant reduces to 1/[equilibrium concentration of monomer] and there is also a set of dimers and trimers in equilibrium with the high linear polymer.

Conclusions

The clean ruthenium catalyzed polymerization of cyclopentene was investigated at different reaction temperatures, catalyst loading and catalyst systems. Higher conversion was observed when the polymerization was performed at lower temperature. Higher cyclopentene conversion (average: 5.7 ± 1.2%) could be achieved with well-defined ruthenium catalyst systems compared to the tungsten systems reported by Calderon. Thus the calculated thermodynamic parameters (ΔH = −5.6 kcal mol^{-1}; ΔS = −18.5 cal mol^{-1} K^{-1}) are lower than those of obtained for the tungsten catalyzed systems (ΔH = −4.4 kcal mol^{-1}; ΔS = −14.9 cal mol^{-1} K^{-1}).[7] Although the equilibrium time is influenced by the catalyst loading or the catalyst activity, the overall cyclopentene conversion, as expected, is determined only by the applied reaction temperature. The equilibrium concentration of monomer does not change when higher amount of catalyst loading (2.5 or 5 times more) or more active catalyst (**3**) were applied. However, these changes influence the polymer molecular weight and PDI values. Longer equilibrium times were observed at lower catalyst loading and temperature. At lower temperature, higher conversion and higher molecular weight polymer could be observed with lower PDI values. The *trans* bond ratios in the polymers fell between 81.8% and 83.8%. This minor difference (which might be within the quantitative ^{13}C NMR measurement error) indicates that *cis*/*trans* ratio is determined by the applied catalyst system rather than the applied reaction temperature in the investigated 0–30 °C temperature range. In conclusion, the cleaner catalysts provide a show significant differences that can be important in the production of polypentenamers for real applications. These values obtained with well-defined systems provide precise definitions of the thermodynamic parameters for this important polymerization reaction.

Acknowledgements

We thank Texas A&M University at Qatar for financial support.

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21 The experimental conditions are the same like in Table 1 described in the ESI† except the temperature (23 °C). The norbornene was added as 0.10 mL toluene-d_8 stock solution (0.113 M) in three portions at 30, 60 and 90 min reaction time. The conversions were determined by ^1H NMR spectrsocopy by the same way described in the general section in the ESI.†

